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# Certificate

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the documents attached hereto are true copies of the Forms P2, P6,  
provisional specification and drawings of South African Patent Application  
No. 2003/1937 in the name of Sasol Technology (Proprietary) Limited ✓

Filed : 10 March 2003 ✓  
Entitled : Extraction of Oxygenates  
from a Hydrocarbon Stream

Geteken te PRETORIA in die Republiek van Suid-Afrika, hierdie dag van  
Signed at in the Republic of South Africa, this 16<sup>th</sup> March 2004  
day of

*J. G. de Jager*  
Registrar of Patents

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FULL NAME(S) OF APPLICANT(S)/PATENTEE(S)								
71	SASOL TECHNOLOGY (PROPRIETARY) LIMITED							
APPLICANTS SUBSTITUTED:						DATE REGISTERED		
71								
ASSIGNEE(S)						DATE REGISTERED		
71								
FULL NAME(S) OF INVENTOR(S)								
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TITLE OF INVENTION								
54	EXTRACTION OF OXYGENATES FROM A HYDROCARBON STREAM							
ADDRESS OF APPLICANT(S)/PATENTEE(S)								
1. STURDEE AVENUE, ROSEBANK, 2196, GAUTENG, SOUTH AFRICA								
ADDRESS FOR SERVICE					S & F REF			
74	SPOOR & FISHER, SANDTON					PA134799/P		
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61								
FRESH APPLICATION BASED ON			DATE OF ANY CHANGE					

SPOOR & FISHER

REPUBLIC OF SOUTH AFRICA  
PATENTS ACT, 1978

REPUBLIC OF SOUTH AFRICA  
REVENUE FORM P.1

APPLICATION FOR A PATENT  
AND ACKNOWLEDGEMENT OF RECEIPT  
(Section 30 (1) – Regulation 22)

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The granting of a patent is hereby requested by the undermentioned applicant on the basis of the present application filed in duplicate

REPUBLIC VAN SUID AFRICA  
S & F REFERENCE

OFFICIAL APPLICATION NO.

21 01

2003/1937

PA134799/P

FULL NAME(S) OF APPLICANT(S)

71

SASOL TECHNOLOGY (PROPRIETARY) LIMITED

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TITLE OF INVENTION

54

SEPARATION OF OXYGENATES FROM A HYDROCARBON STREAM

THE APPLICANT CLAIMS PRIORITY AS SET OUT ON THE ACCOMPANYING FORM P.2. THE EARLIEST PRIORITY CLAIM IS:

COUNTRY: NIL

NUMBER: NIL

DATE: NIL

THIS APPLICATION IS FOR A PATENT OF ADDITION TO PATENT APPLICATION NO.

21 01

THIS APPLICATION IS A FRESH APPLICATION IN TERMS OF SECTION 37 AND IS BASED ON APPLICATION NO.

21 01

THIS APPLICATION IS ACCCOMPANIED BY:

- 1. A single copy of a provisional specification of 8 pages.
- 2. Drawings of 1 sheet.
- 3. Publication particulars and abstract (Form P.8 in duplicate).
- 4. A copy of Figure of the drawings (if any) for the abstract.
- 5. Assignment of invention.
- 6. Certified priority document.
- 7. Translation of the priority document.
- 8. Assignment of priority rights.
- 9. A copy of the Form P.2 and the specification of S.A. Patent Application No .
- 10. Declaration and power of attorney on Form P.3.
- 11. Request for ante-dating on Form P.4.
- 12. Request for classification on Form P.9.
- 13. Form P.2 in duplicate.
- 14. Other.

74 ADDRESS FOR SERVICE: SPOOR & FISHER, SANDTON

Dated: 10 March 2003

  
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PATENT ATTORNEYS FOR THE APPLICANT(S)

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## PROVISIONAL SPECIFICATION

(Section 30(1) – Regulation 27)

OFFICIAL APPLICATION NO.

21	01	2003/1937
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LODGING DATE

22	10 MARCH 2003
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FULL NAMES OF APPLICANTS

71	SASOL TECHNOLOGY (PROPRIETARY) LIMITED
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FULL NAMES OF INVENTORS

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TITLE OF INVENTION

54	SEPARATION OF OXYGENATES FROM A HYDROCARBON STREAM
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## **EXTRACTION OF OXYGENATES FROM A HYDROCARBON STREAM**

### **BACKGROUND OF THE INVENTION**

This invention relates to a method for extracting oxygenates from a hydrocarbon stream.

Many methods for extracting oxygenates from hydrocarbon streams are known. Such extraction methods include hydrogenation, azeotropic distillation, extractive distillation, vapour phase dehydration, liquid phase dehydration and liquid-liquid extraction.

This invention relates to a process for extracting or separating oxygenates from the condensation product of a low temperature Fischer-Tropsch reaction, to produce a condensation product that is particularly suitable for the production of linear alkyl benzene.

### **SUMMARY OF THE INVENTION**

According to the invention there is provided a method for extracting oxygenates from the condensation product of a low temperature Fischer-Tropsch reaction containing 15% to 30% by weight olefins, typically less than 25% by weight olefins, 60% to 80% by weight paraffins and 5% to 10% by weight oxygenates, while preserving the olefin content of the condensation product. The oxygenate extraction process being a liquid-liquid extraction process using dry methanol or a mixture of methanol and water, preferably a mixture of methanol and water, as the solvent.

The liquid-liquid extraction process preferably takes place in a liquid extraction column.

Preferably, a raffinate from the extraction column is sent to a stripper column from which a hydrocarbon feed stream containing olefins and paraffins and typically less than 0.01% by weight oxygenates exits as a bottoms product, and methanol exiting from the top of the stripper column is preferably recycled to the extraction column.

An extract from the extraction column is sent to a recovery column from which oxygenates and water exit as a bottoms product and methanol exits as a tops product, with the methanol from the tops product and water from the bottoms product preferably being recycled to the extraction column.

#### BRIEF DESCRIPTION OF THE DRAWING

The Figure is a block diagram of a process of the invention for extracting oxygenates from a hydrocarbon stream.

#### DESCRIPTION OF PREFERRED EMBODIMENTS

This invention relates to a process for extracting oxygenates from a hydrocarbon condensate stream from a low temperature Fischer-Tropsch reaction. The substantially oxygenate-free hydrocarbon stream can be used in the production of linear alkyl benzene.

In the Fischer-Tropsch process, synthesis gas (carbon monoxide and hydrogen) obtained either from the gasification of coal or the reforming of natural gas, is reacted over a Fischer Tropsch catalyst to produce a mixture of hydrocarbons ranging from methane to waxes and smaller amounts of oxygenates.

In a low temperature Fischer-Tropsch reaction, the reaction takes place in a slurry bed reactor or fixed bed reactor, preferably a slurry bed reactor, at a temperature in the range of 160°C - 280°C, preferably 210°C - 260°C, and a pressure in the range of 18-50 bar (gauge), preferably between 20-30 bar (gauge), in the presence of a catalyst. The catalyst may include iron, cobalt, nickel or ruthenium. However, a cobalt-based catalyst is preferred for the low temperature reaction. Usually, the cobalt catalyst is supported on an alumina support.

During the Fischer-Tropsch reaction, a lighter hydrocarbon vapour phase is separated from a liquid phase comprising heavier liquid hydrocarbon products. The heavier liquid hydrocarbon product (waxy products) is the major product of the reaction and may, for example, be hydrocracked to produce diesel and naphtha.

The lighter hydrocarbon vapour phase which comprises gaseous hydrocarbon products, unreacted synthesis gas and water is condensed to provide a "condensation product" which comprises an aqueous phase and a hydrocarbon condensation product phase.

The hydrocarbon condensation product includes olefins, paraffins in the C<sub>4</sub> to C<sub>28</sub> range, and oxygenates including alcohols, esters, aldehydes, ketones and acids.

Typically, a hydrocarbon condensation product for a low temperature Fischer-Tropsch reaction contains 15%-30% by weight olefins, 60%-80% by weight paraffins, and 5%-10% by weight oxygenates. It has, surprisingly, been found that even though this condensation product has a low olefin content, it can be used in the production of linear alkyl benzene. However, it is necessary to first extract the oxygenates as these species have a negative effect on the alkylation reaction. There is therefore a need to find a process for extracting oxygenates, but at the same time preserve the olefin concentration. For the production of linear alkyl benzene, the hydrocarbon condensate product is fractionated into a C<sub>10</sub> - C<sub>13</sub> cut which, by way of

example, contains 22% by weight olefins, 71% by weight paraffins and 7% by weight oxygenates. As mentioned above, the oxygenates need to be extracted to provide a product fit for production of linear alkyl benzene.

In the prior art, many methods of extracting oxygenates from hydrocarbon streams are suggested. Such removal methods include hydrogenation, azeotropic distillation, extractive distillation, vapour phase dehydration, liquid phase dehydration and liquid-liquid extraction. It has been found that liquid-liquid extraction is a preferred method of oxygenate extraction because, if the correct solvent is selected, the olefin concentration can be preserved. In liquid liquid extraction, the solvent can be any polar material that has partial miscibility with the feed stream 14, such as tri-ethanol amine, tri-ethylene glycol with between zero and 20% water, acetonitrile with between 5% and 20% water, acetol, diols, methanol, or ethanol and water. A combination of the above solvents is also possible. Normally, a high-boiling point solvent is preferred because the solvent recovery steps after extraction requires less energy than will be the case for a low-boiling point solvent. However, it has been found that dry methanol, or a mixture of methanol and water, which is a low-boiling point solvent, need not suffer from this drawback, because it can be effective at low solvent to feed ratios (this can be lower than 1:1 if the required oxygenate extraction is not too severe). Furthermore, one would not expect to be able to use methanol and water as a solvent in a liquid-liquid extraction column to extract oxygenates from the abovementioned hydrocarbon condensate because a study of the different azeotropes with water that exist in the hydrocarbon condensate would lead one to expect that it would not be possible to distil water in a solvent recovery column without azeotroping oxygenates overhead as well. Surprisingly, this turns out not to be the case.

With reference to the Figure, a liquid-liquid extraction process of the invention includes an extraction column 20. The fractionated condensation product of a low temperature Fischer-Tropsch reaction described above 14 is fed into the extraction column 20 at, or near, the bottom thereof and a solvent stream 21 comprising methanol or a mixture

of methanol and water is fed into the extraction column 20 at or near the top thereof.

Raffinate 22 from the top of the extraction column 20, which includes olefins and paraffins and a small amount of solvent, enters a raffinate stripper column 23 and a hydrocarbon feed stream olefins, paraffins and less than 0.01% by weight oxygenates exits as a bottoms product 24, while solvent exits as a tops product 25 and is returned to the solvent feed stream 21. If it is desired to recover the bottoms product 24 as a vapour stream, this can be done by adding a vapour side draw to the column just above the reboiler. The liquid product from the reboiler will then be a very small effluent stream.

An extract 26 is drawn from the bottom of the extraction column 20 and is fed to solvent recovery column 27. Oxygenates exit as a bottoms product 28 from the solvent recovery column 27, while solvent exits as a tops product 29 and is recycled to the solvent stream 21. The oxygenate content of the tops product 29 can be as low as 50 ppm, depending on the solvent to feed ratio used in the extraction column 20.

As mentioned above, normally, a high-boiling solvent is preferred for liquid-liquid extraction because the solvent recovery steps after extraction requires less energy than will be the case for a low-boiling solvent. However, it has been found that dry methanol, or a mixture of methanol and water, which is a low-boiling solvent, need not suffer from this drawback, because it can be effective at low solvent to feed ratios (this can be lower than 1:1 if the required oxygenate extraction is not too severe).

A study of the different azeotropes that exist between components in the feed and water would lead one to expect that it would not be possible to distil water overhead in the solvent recovery column 27 without azeotroping oxygenates overhead as well. Surprisingly, this turns out not to be the case. Methanol, which does not form azeotropes with any of the other species present, prevents the water/oxygenate azeotropes from distilling

over at the same temperature as the paraffins and olefins. This appears to be due to an extractive distillation effect. Additionally, it is possible to distil the paraffins and olefins overhead, while recovering all the oxygenates as bottom products (this is not possible for a dry methanol system, because only a fraction of the paraffins and olefins can be distilled overhead without carrying over oxygenates in a dry methanol system). This has the effect of enhancing the overall paraffin and olefin recovery of the process, because the overheads 29 of the solvent recovery column 27 is recirculated to the extraction column 20, which means that the paraffins and olefins will be forced to leave the process in the product stream 24.

It is therefore possible to have a pure hydrocarbon (paraffin and olefin) stream 24, and a pure oxygenate and water stream 28 as products from the process, without the use of a counter solvent in the extraction column. In this mode of operation, all the methanol, and part of the water (10-50%) are also recovered in the overhead stream 29.

Because the bottoms product 28 contains a high percentage of water (10-60%), this stream will form two liquid phases that can be decanted in a decanter 30. The organic phase will be a pure oxygenate stream 31, which leaves the process as a product. The aqueous phase will be stream 32, which can be recycled to the extraction column 20. This stream can either enter the extraction column at the top along with the solvent stream 21, or slightly lower down the column 20, to prevent the low amount of oxygenates that will be present in this stream from appearing in the raffinate stream 22.

It is also possible to run the extraction column 20 and the solvent recovery column 27 at different methanol / water ratios. This may be desirable because a high water content in the extraction column 20 will lead to increased solvent to feed ratios (because of reduced solubility of oxygenates in the solvent), while a certain amount of water is necessary to achieve the extractive distillation effect in combination with methanol to recover all the paraffins and olefins as overhead products in the solvent recovery column 27. The different methanol / water ratios in the two

columns (20 and 27) can be achieved by diverting some of the water in stream 32 to stream 26 by means of a stream 33.

After passing the C<sub>10</sub> – C<sub>13</sub> hydrocarbon feed stream mentioned above through the abovementioned oxygenate extraction process using a mixture of methanol (95% by weight) and water (5% by weight) and a solvent to feed ratio of 1.2:1, the purified hydrocarbon feed stream contains 23% by weight olefins, 77% by weight paraffins and less than 0.01% by weight oxygenates. Not only does the extraction process extract oxygenates, it also preserves the olefin content of the hydrocarbon feed. The purified hydrocarbon feed stream containing olefins is particularly useful in the production of linear alkyl benzene.

#### EXAMPLE

The tables on the following pages set out a mass balance for a typical extraction process according to the invention. The results are by way of example only and do not limit the scope of the invention. The numbering system of the unit operations and flow streams correspond to the numbering system in the Figure.

#### Extraction column 20:

Stream	14		21		22		26	
	Comp (wt%)	Flow (kg/hr)	Comp (wt%)	Flow (kg/hr)	Comp (wt%)	Flow (kg/hr)	Comp (wt%)	Flow (kg/hr)
Total	100.00	3000	100.00	3000	100.00	2729	100.00	3270
Total C <sub>10</sub> -C <sub>13</sub> olefins/paraffins	92.34	2770	0.000	0.000	96.99	2647	3.764	123.1
Total oxygenates	7.230	216.9	0.000	0.000	0.1477	4.033	6.509	212.8
Lights and Heavies	0.4087	12.26	0.000	0.000	0.4204	11.47	0.02394	0.783
Water	0.01127	0.338	5.000	150.0	0.0437	1.195	4.560	149.1
Methanol	0.000	0.000	95.00	2850	2.394	65.34	85.14	2784

In stream 14 the paraffin/olefin content is 69.34% by weight paraffins and 23% by weight olefins.

Raffinate Stripper column 23:

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Stream	25	24		
	Comp (wt%)	Flow (kg/hr)	Comp (wt%)	Flow (kg/hr)
Total	100.00	65.60	100.00	2663
Total C10-C13 olefins/paraffins	3.647	2.393	99.29	2645
Total oxygenates	0.001524	0.001	0.1513	4.03
Lights and Heavies	0.07163	0.047	0.4291	11.43
Water	1.658	1.088	0.004016	0.107
Methanol	94.62	62.08	0.1226	3.267

In stream 24 the paraffin/olefin content is 74% to 77% by weight paraffins and 23% to 26% by weight olefins.

Solvent recovery column 27 :

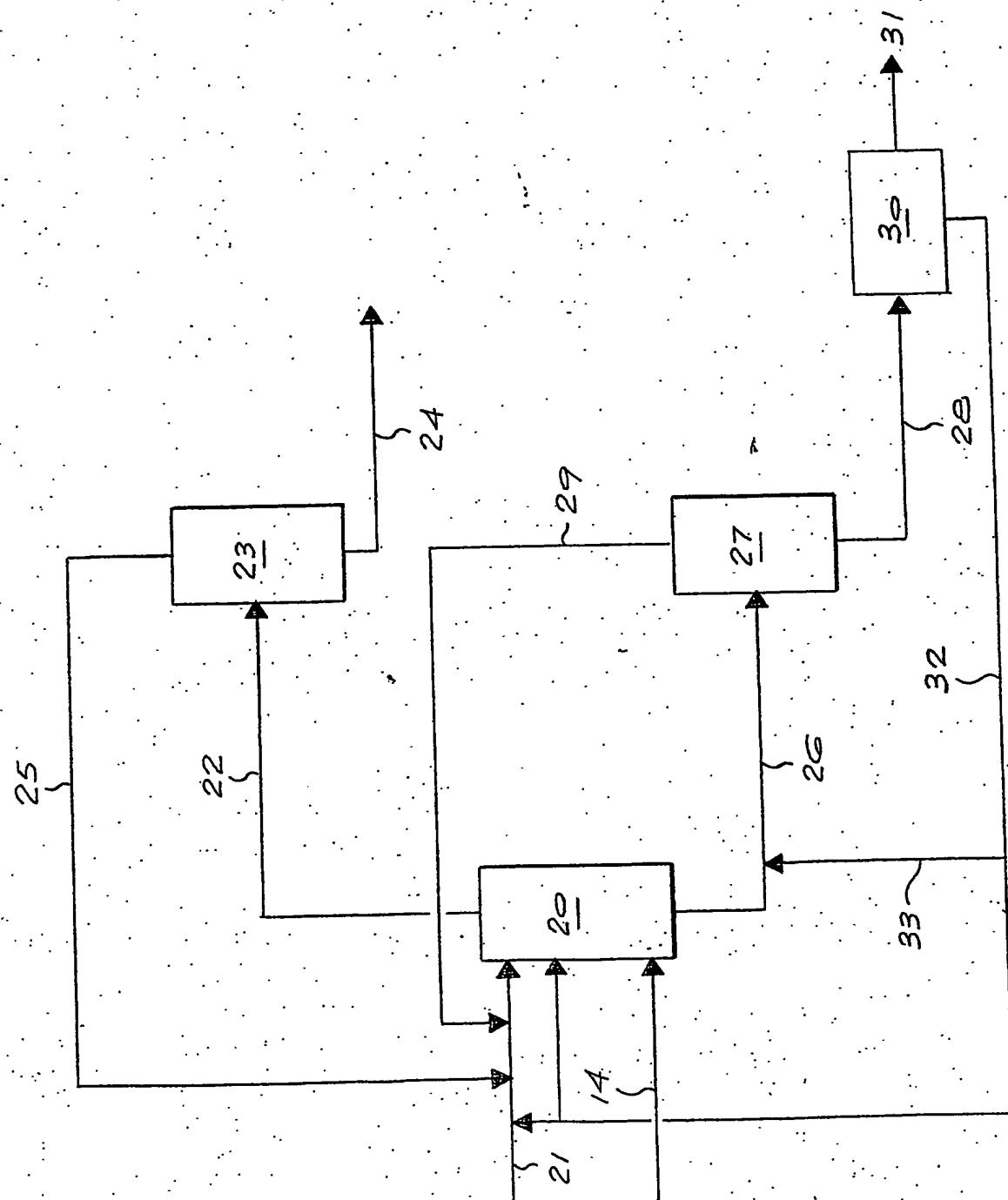
Stream	29	28		
	Comp (wt%)	Flow (kg/hr)	Comp (wt%)	Flow (kg/hr)
Total	100.00	2945	100.00	324.8
Total C10-C13 olefins/paraffins	3.726	109.7	4.115	13.37
Total oxygenates	0.009981	0.294	65.44	212.6
Lights and Heavies	0.02664	0.785	0.000	0.000
Water	1.705	50.24	30.44	98.89
Methanol	94.53	2784	0.000	0.000

Dated this 10<sup>TH</sup> day of March 2003.

Spoor & Fisher

Applicant's Patent Attorneys

sol Technology (Proprietary) Limited  
provisional Application



*[Handwritten Signature]*  
SIMPSON & FISHER

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